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Wine ethanol ^{14}C as a tracer for fossil fuel CO_2 emissions in Europe: Measurements and model comparison

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[1] ^{14}C (radiocarbon) in atmospheric CO_2 is the most direct tracer for the presence of fossil-fuel-derived CO_2 (CO_2-ff). We demonstrate the ^{14}C measurement of wine ethanol as a way to determine the relative regional atmospheric CO_2-ff concentration compared to a background site (''regional CO_2-ff excess'') for specific harvest years. The carbon in wine ethanol is directly back traceable to the atmospheric CO_2 that the plants assimilate. An important advantage of using wine is that the atmosphere can be monitored annually back in time. We have analyzed a total of 165 wines, mainly from harvest years 1990–1993 and 2003–2004, among which is a semicontinuous series (1973–2004) of wines from one vineyard in southwest Germany. The results show clear spatial and temporal variations in the regional CO_2-ff excess values. We have compared our measured regional CO_2-ff excess values of 2003 and 2004 with those simulated by the REgional MOdel (REMO). The model results show a bias of almost +3 parts per million (ppm) CO_2-ff compared with those of the observations. The modeled differences between 2003 and 2004, however, which can be used as a measure for the variability in atmospheric mixing and transport processes, show good agreement with those of the observations all over Europe. Correcting for interannual variations using modeled data produces a regional CO_2-ff excess signal that is potentially useful for the verification of trends in regional fossil fuel consumption. In this fashion, analyzing ^{14}C from wine ethanol offers the possibility to observe fossil fuel emissions back in time on many places in Europe and elsewhere.

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1. Introduction

[2] CO_2 emitted by the combustion of fossil fuels (CO_2-ff) is worldwide the largest net carbon flux to the atmosphere. In densely populated and industrialized regions such as Europe, this net source overwhelms the natural net sources and sinks [*Levin and Karstens*, 2007a]. If under these circumstances one still wants to quantify the net exchange of CO_2 by the biosphere and coastal seas, accurate knowledge about the spatial and temporal behavior of CO_2-ff is essential. In the case of Europe, both detailed, reliable statistical data about fossil fuel combustion, and atmospheric measurements of the CO_2-ff concentration are therefore indispensable. Determination of the amount of CO_2-ff is also of crucial importance by itself: emission reductions in the framework of the Kyoto Protocol should be independently verified, and a robust and accurate verification tool is important for policy-makers and -thus- for society.

[3] The atmospheric CO_2-ff concentration cannot be deduced directly from atmospheric CO_2 measurements, because it cannot be distinguished from CO_2 released by other sources (e.g., the biosphere). Other measurements are therefore needed to identify and quantify atmospheric CO_2-ff concentrations. The measurement of ^{14}C in air and plant samples has proven to be a very useful tracer for atmospheric CO_2-ff [*Suess*, 1955; *Levin et al.*, 1989, 2003; *Turnbull et al.*, 2006; *Hsueh et al.*, 2007; *Levin and Rödenbeck*, 2007]. SF_6 and CO have been investigated recently as ''surrogate'' tracers for CO_2-ff [*Turnbull et al.*, 2006; *Gamnitzer et al.*, 2006; *Levin and Karstens*, 2007b], but ^{14}C is the only direct tracer available. Since CO_2-ff contains no ^{14}C, the atmospheric $^{14}CO_2$ concentration is diluted when CO_2-ff is added to the atmosphere. Other (current) CO_2 sources do not dilute or concentrate the regional/local atmospheric $^{14}CO_2$ concentration to such a significant extent as CO_2-ff and therefore the rate of dilution compared to a background location can be used as a relative measure for local and/or regional CO_2-ff concentrations (mentioned in the text as ''regional CO_2-ff excess'' and in equations as ''CO_2-ffx'').

[4] $^{14}CO_2$ is currently measured on a regular basis in air samples (continuous bi-weekly or monthly integrated) of less than 10 measurement sites in Europe (beside our own measurement site Lutjewad in the Netherlands, the sites mentioned by *Levin et al.* [2008] and *Kuc et al.* [2007]). Therefore little data and knowledge is available about

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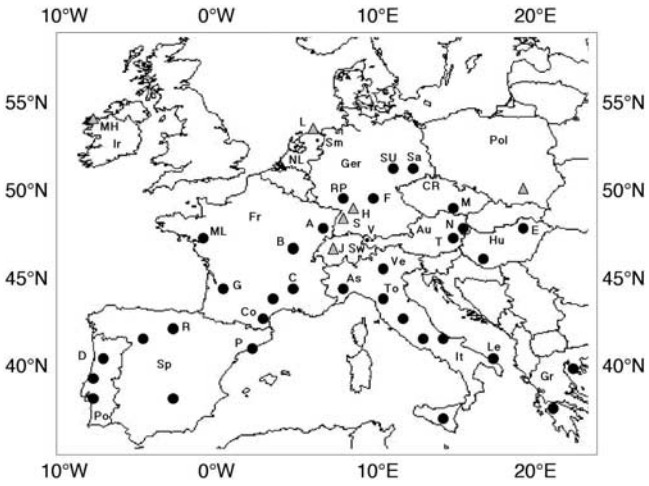

Figure 1. Investigated wine regions (big black dots) and current (gray triangles) and former (small black dots) atmospheric measurement sites. The regions/cities and sites mentioned in the text or in other figures are labeled. Ir, Ireland: MH, Mace Head; Po, Portugal: D, Douro; Sp, Spain: P, Penedes, which also labels the city Barcelona; R, Rioja, which also labels the nuclear power plant of Santa Maria de Garona; Fr, France: ML, Maine-et-Loire; A, Alsace; B, Bourgogne; Co, Corbieres; and G, Gironde, which also labels the city Bordeaux; C, Côtes-du-Rhône, which also labels the nuclear power plants of Tricastin and Cruas; NL, Netherlands: L, Lutjewad; and Sm, Smilde; Ger, Germany: SU, Saale-Unstrut; Sa, Sachsen; F, Franken; H, Heidelberg; S, Schauinsland; and Rheinland-Pfalz (RP), which also labels the village Birkweiler; CR, Czech Republic: M, Moravia; Sw, Switzerland: J, Jungfraujoch; Au, Austria: N, Neusiedlersee; T, Thermenregion; and Vermunt (V); Hu, Hungary: E, Eger; and It, Italy: As, Asti; Ve, Verona; To, Toscana; and Le, Lecce, which also labels the city Lecce. The sites of Poland (Pol) and Greece (Gr) have not been mentioned specifically in the text.

spatial and temporal differences in the regional CO_2-ff excess within Europe and more representative measurement sites of atmospheric $^{14}CO_2$ are needed in which long-term trends can be monitored. Since setting up and maintaining an air measurement site is labor and cost intensive, we have started the analysis of ^{14}C in wine ethanol of different European regions to supplement the monitoring network in Europe in an easy and relatively cheap way. Several studies already showed that ^{14}C in (annual) plant materials like corn leaves [*Hsueh et al.*, 2007], rice [*Shibata et al.*, 2005], grape wine ethanol [*Burchuladze et al.*, 1989], grass [*Quarta et al.*, 2005], tree leaves [*Levin et al.*, 1980] and tree rings [*Tans et al.*, 1979; *Levin and Kromer*, 1997], sampled by the plant during the photosynthesis process and until it was harvested, is a reliable tracer of atmospheric $^{14}CO_2$ concentrations of the respective growing period. Although the use of ^{14}C from plant material as a proxy for atmospheric $^{14}CO_2$ is not ideal (as we discuss in section 4 of this paper) and each plant material has its own advantages and disadvantages, we choose wine ethanol as sample material because, (1) wines are easy to obtain (in a local wine store or supermarket), (2) the wine grapes grow at many different locations in Europe, (3) contrary to air samples and most annual plant materials, previous sampling years can still be measured: trends in atmospheric $^{14}CO_2$ and in the regional CO_2-ff excess (if $^{14}CO_2$ data of a background site are available) can be monitored back in time and (4) we already had an archive of 128 ^{14}C-measured wine ethanol samples. The measured $\Delta^{14}C$ in wine ethanol represents the atmospheric $\Delta^{14}C$ value, because atmospheric CO_2 has been transformed into sugars in the grape leaves, which are almost immediately transported to the grape berries [*Hale and Weaver*, 1962; *Koblet*, 1975; *Alleweldt*, 1977; *Alleweldt et al.*, 1975; *Coombe*, 1992]. The sugars in the grape berries have been transformed into ethanol in the wine making process.

[5] In this paper we first show that our measurements of ^{14}C in wine ethanol samples agree well with air measurements in Europe. Secondly, we demonstrate the spatial and temporal variations in the regional CO_2-ff excess (relative to background site Vermunt, Austria in the period until 1985 and Jungfraujoch, Switzerland in the period 1985–2004) of the different investigated European wine regions based on our wine results. thirdly, we present a comparison between the measured regional CO_2-ff excess of the different wine regions and the regional CO_2-ff excess as simulated for 2003 and 2004 with regional atmospheric transport model REMO using different CO_2-ff emission inventories. From this comparison we conclude how to use the model-corrected measurements for trend analysis in fossil fuel consumption.

2. Experimental

2.1. Wine Samples

[6] We have measured ^{14}C in wine ethanol of 165 different wines from 32 different regions in 9 different European countries (Figure 1). The wines were bought in supermarkets, wine stores and, in one case, directly from the local producer (Rheinland-Pfalz region, southwest Germany). On the basis of the information on the label of the wine bottle, we selected non-mixed wines (of one region, one harvest year and of one wine-farmer). We have investigated wines from different harvest years and mainly from the periods 1990–1993 and 2000–2004. The different wine regions have not been measured with the same frequency. The investigated German Rheinland-Pfalz wines have harvest years in the period 1965–2004. Many of the Rheinland-Pfalz wines originated from one and the same vineyard near the village Birkweiler (22 different harvest years in period 1973–2004).

2.2. Measurement of $\Delta^{14}C$ in Wine Ethanol

[7] In the period 1993–2007, 128 wine ethanol samples have been analyzed on ^{14}C at the Centre for Isotope Research (CIO) Groningen using a method in which, after complete distillation of wine ethanol form the wine, wine ethanol is first combusted and oxidized to CO_2 and then measured with a low background proportional gas counter [*Mook and Streurman*, 1983; *van der Plicht et al.*, 1992]. The obtained $\Delta^{14}C$ data are given relative to the activity of the international certified oxalic acid calibration material, and are corrected by convention for fractionation ($\delta^{13}C$) and decay [*Stuiver and Polach*, 1977]. The $\Delta^{14}C$ sample data are expressed as ‰ (per mil) deviation from this calibration

material. Samples are analyzed four times to increase the total number of counts and thus decrease the statistical uncertainty (Poisson statistics). The combined uncertainty (or accuracy) of the mean $\Delta^{14}C$ value of an individual sample is 2–3‰.

[8] In 2007, 40 wine ethanol samples have been analyzed on ^{14}C using the ^{14}C dedicated Accelerator Mass Spectrometer (AMS) at the CIO, Groningen. After distillation of a few milliliter ethanol from a wine, the ethanol was first combusted and oxidized to CO_2 and then graphitized and pressed into targets as described by *Aerts-Bijma et al.* [1997, 2001]. All sample targets (two targets per wine ethanol sample) have been measured twice in two different batches using the AMS system [*van der Plicht et al.*, 2000]. Background samples (anthracite) and standards (certified oxalic acid) have been measured in every batch as part of the calibration and quality control procedures. The fractionation and decay corrected $\Delta^{14}C$ value of a wine ethanol sample is calculated as the weighted average value of the (max. 4) individual measurements. In this way, we can achieve a combined uncertainty that is mostly below 3‰ [*Meijer et al.*, 2006]. The results of both used analysis methods agree very well (within the measurement uncertainty: ±3‰).

2.3. Calculation of the Regional Atmospheric CO_2-ff Excess From $\Delta^{14}C$ in Wine Ethanol

[9] The regional atmospheric CO_2-ff excess at a particular measurement site compared to a background site is derived from ^{14}C measurements by using two mass balance equations, which describe the atmospheric mixing ratios of CO_2 (equation (1)) and of $\Delta^{14}C$ (equation (2)) at the measurement site. This approach is to some extent the same as described by *Zondervan and Meijer* [1996], *Levin et al.* [2003], *Turnbull et al.* [2006], and *Levin and Rödenbeck* [2007].

$$CO_2(site) = CO_2(bg) + CO_2(bio) + CO_2(oc) + CO_2(x) + CO_2(ffx) \quad (1)$$

$$\Delta^{14}C(site) = \Delta^{14}C(bg) \bullet \frac{CO_2(bg)}{CO_2(site)} + \Delta^{14}C(bio) \bullet \frac{CO_2(bio)}{CO_2(site)} + \Delta^{14}C(oc) \bullet \frac{CO_2(oc)}{CO_2(site)} + \Delta^{14}C(x) \bullet \frac{CO_2(x)}{CO_2(site)} + \Delta^{14}C(ffx) \bullet \frac{CO_2(ffx)}{CO_2(site)} \quad (2)$$

The CO_2 concentration and the $\Delta^{14}C$ value measured at a specific site consist of the mixing ratio in the free troposphere ("bg", background), the regional biosphere components ("bio", photosynthesis and heterotrophic respiration), the regional ocean component ("oc"), unknown regional components ("x", for instance $^{14}CO_2$ emitted by nuclear power plants or CO_2 released by the burning of biomass) and, last but not least, the regional fossil fuel component ("ffx": regional CO_2-ff excess). The relative contribution of each component to the total atmospheric CO_2 concentration and $\Delta^{14}C$ value at a measurement site is time and location-specific.

[10] The regional CO_2-ff excess (in our definition this can also be a negative value: deficit) at a measurement site compared to a background site can be calculated from equation (2). Since we only had data for $\Delta^{14}C$(ffx) (which is always −1000‰), $\Delta^{14}C$ (site), $\Delta^{14}C$ (bg) and CO_2 (bg), we have made a few assumptions about the other parameters mentioned in this equation. With the assumption:

$$CO_2(site) \approx CO_2(bg) + CO_2(ffx) \quad (3)$$

and the assumption that the regional biosphere, ocean and unknown CO_2-sources and sinks have not contributed significantly to the measured $\Delta^{14}C$ value at a site, we have calculated the regional CO_2-ff excess according to:

$$CO_2(ffx) \approx \frac{CO_2(bg) \bullet \left(\Delta^{14}C(site) - \Delta^{14}C(bg)\right)}{\left(\Delta^{14}C(ffx) - \Delta^{14}C(site)\right)} \quad (4)$$

In our approach a regional CO_2-ff excess of 1 ppm at a measurement site corresponds with a difference between the $\Delta^{14}C$ values of the measurement site and the background site of −5.6‰ in 1965 to −2.8‰ in 2004. The difference in time is related to the decreased atmospheric background $\Delta^{14}C$ value after the ban treaty for aboveground nuclear bomb tests in 1963, because of oceanic and biosphere carbon exchange and (partly) global CO_2-ff emissions [*Levin and Hesshaimer*, 2000; *Randerson et al.*, 2002].

[11] The assumptions leading from equations (1) and (2) to equations (3) and (4), but also some other assumptions we have made to calculate the regional CO_2-ff excess, are not at all as crude as they seem to be at first sight. Still, some of the assumptions may have a significant effect on our final results, especially in regions with relatively small regional CO_2-ff excess (<1 ppm) and therefore we will discuss and estimate (if possible) the effects.

[12] In our approach we do not have data for "CO_2 (site)", which is needed to calculate the regional CO_2-ff excess using equation (2) and is also used in other studies in which the regional CO_2-ff excess has been calculated [*Levin et al.*, 2003; *Turnbull et al.*, 2006]. We have therefore approximated this CO_2 concentration according to equation (3). The average contribution of "oc" and "bio" to the total CO_2 concentration that the wine plants experience during daytime in the growing season (the time they assimilate CO_2) is relatively low: thanks to the well-mixed atmosphere under these circumstances the conditions the wine plants experience are relatively close to background [*Levin et al.*, 1995]. As CO_2 background concentrations for the period 1965–2004 we used the weighted monthly mean CO_2 concentrations measured at Mauna Loa (Hawaii, 19°32′N, 155°34′W, 3397 m asl) and published by *Keeling and Whorf* [2005], because no other available data sets of background sites representing the free continental troposphere of Europe were found for this specific time period. Mauna Loa is an elevated marine site, which will not fully represent the background of all our continental measurement sites, where different continental sources and sinks (mainly biosphere and fossil fuel emissions) affect the free troposphere CO_2 concentrations. On the basis of studies about spatial and temporal differences in CO_2 concentration by *Levin et al.* [1995], *Chevillard et al.* [2002b], and *Schmidt et al.* [2003],

we have estimated the effect of our approach, in which we neglect regional biosphere and ocean contributions to the CO_2 background concentration and use Mauna Loa as background site, on the calculated regional CO_2-ff excess. If "CO_2 (site)" in our assumption (equation (3)) is over- or underestimated by maximal ±20 ppm, a calculated regional CO_2-ff excess of 10 ppm will deviate maximal ±0.65 ppm ("+" when overestimated) and a regional CO_2-ff excess of 1 ppm maximal ±0.06 ppm.

[13] The second main assumption we have made in the calculation of the regional CO_2-ff excess is that the regional biosphere, ocean and unknown CO_2-sources and sinks have not contributed significantly to the measured difference between the $\Delta^{14}C$ value at a site and a background site, because the $\Delta^{14}C$ values of these regional sources and sinks are (in general) relatively close to the background value (which is, as example: +71‰ in May–October 2003, Swiss High Alpine Research station Jungfraujoch [*Levin and Kromer*, 2004]). The $\Delta^{14}C$-ff value (−1000‰), however, is far more different from the background value and therefore the contribution of the regional CO_2-ff excess to the total $\Delta^{14}C$ value at a measurement site (equation (2)) is relatively large.

[14] The effect of our assumption on the calculated regional CO_2-ff excess can (partly) be estimated based on model calculations of other researchers. *Turnbull et al.* [2006] observed, based on the use of simulated heterotrophic respiration data a deviation of maximal +0.5 ppm CO_2-ff when no correction was made for this respiration ($\Delta^{14}C$ value used for 2003 data: 166 ± 100‰ [*Turnbull et al.*, 2006]). *Levin and Rödenbeck* [2007] also correct for this anomaly based on model simulations. The ocean exchange has a minor influence on the atmospheric $\Delta^{14}C$ value, especially at continental sites, based on the work of *Hsueh et al.* [2007] who simulated this for North America (data of 2004). Only at coastal sites a "regional CO_2 (oc) excess" of maximal 1‰ was found and for these sites the calculated regional CO_2-ff excess according to our approach would be overestimated approximately by 0.35 ppm (based on CO_2 (site) ≈ 380 ppm and $\Delta^{14}C$(bg) ≈ 66‰). Since these model calculations are based on 2003 and 2004, it should be mentioned that we did not investigate whether these results are also representative for especially the period 1965–1990, when the atmospheric $\Delta^{14}C$ value (780–150‰) was much higher than currently and large variations in the $\Delta^{14}C$ values were visible because of the biosphere and ocean exchange [*Randerson et al.*, 2002]. In this period the $\Delta^{14}C$ values of the regional biosphere and ocean might have been significantly different from the background and might have had a far more important influence on the measured $\Delta^{14}C$ value at a site than currently.

[15] In our assumptions we have ignored the influence of the unknown components "x" on the atmospheric $\Delta^{14}C$ value and CO_2 concentration at a measurement site, since these are difficult to identify or quantify. In the analysis of the data, however, we have been aware of the possible influences of, for instance, nearby ^{14}C emitting nuclear power plants.

[16] As background $\Delta^{14}C$ values we used data of the Austrian Vermunt station (47°4′N, 9°34′E, 1800 m asl; summer mean results: May–August) for the investigated wines of 1965–1985 and data of the High Alpine Research station Jungfraujoch (Swiss Alps, 46°33′N, 7°59′E, 3450 m asl; weighted monthly mean results of bi- weekly integrated atmospheric CO_2 samples) for the period 1985–2004 as published by *Levin and Kromer* [2004]. We obtained the $\Delta^{14}C$ values of Jungfraujoch in 2004 from *Levin et al.* [2008]. The $\Delta^{14}C$ data of both sites do overlap only for the summer period (May–August) of 1986. In that year the $\Delta^{14}C$ values differ only by 1‰, which is very well comparable within the internal measurement precisions (±5–8‰ for Vermunt and 2–4‰ for Jungfraujoch [*Levin and Kromer*, 2004]). We have assumed that both these measurement locations represent the free troposphere for all our measurement sites and are not significantly influenced by variable local/regional CO_2 sources and sinks. However, the background sites represent mainly "continental" sites where the effect of the $^{14}CO_2$ from the ocean is relatively small [*Levin and Hesshaimer*, 2000], and mountain venting at sites like Jungfraujoch [*Henne et al.*, 2005] adds a variable regional CO_2 excess to the free tropospheric background CO_2 concentration at the background site itself. These effects, which are difficult to determine but could influence (part of) our results, will be taken into consideration in the discussion of our results (section 2.5).

[17] We have calculated the regional CO_2-ff excess for the period in which the wine grapes of all our investigated wines will in general have sampled atmospheric CO_2. This is annually a period of approximately 6 weeks between July and the end of October. When exactly depends on the wine region, the grape sorts and the weather conditions [*Alleweldt*, 1977; *van Leeuwen et al.*, 2004], but for the majority of our wines this period is in August and September. To approach this sampling time period of the grapes for the used background CO_2 concentration and background $\Delta^{14}C$ value for every investigated harvest year, we have chosen to use the averages of the (monthly) mean values over the period July–October with extra (three-fold) weight for August and September. The relative standard deviation of these average monthly mean values was for the period 1965–2004, 0.4% for the average CO_2 concentrations of Mauna Loa (319–375 ppm), unknown for the mean summer $\Delta^{14}C$ values of Vermunt (780–190‰) and 1.4% for the average $\Delta^{14}C$ values of Jungfraujoch (192–59‰). The uncertainties in the used average background values (the standard deviation can be used as a measure for that), especially in the $\Delta^{14}C$ values, introduce an uncertainty in the calculated regional CO_2-ff excess of a measurement site. Because the calculation of the regional CO_2-ff excess is based on the absolute difference in the $\Delta^{14}C$ value between the measurement site and the background site (equation (4)), the absolute uncertainty in the background $\Delta^{14}C$ is a main factor of influence. We have calculated the uncertainty in the regional CO_2-ff excess of 1965, 1986 and 2004 based on the relative standard deviation in the average $\Delta^{14}C$ values at Jungfraujoch (also used for Vermunt). The uncertainty (1 sigma) in the calculated regional CO_2-ff excess (1–10 ppm) is ≈2 ppm in 1965, ≈1.2 ppm in 1986 and ≈0.75 ppm in 2004.

2.4. Experimental Results

[18] Figure 2 shows the temporal trend of the annual average $\Delta^{14}C$ values in the period July–October (weighted as described in the previous section) in air samples of different measurement sites in Europe [*Levin and Kromer*,

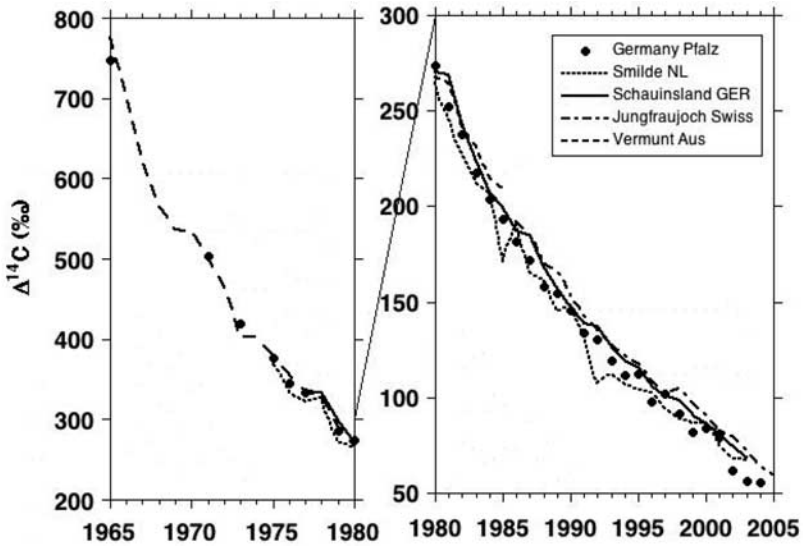

Figure 2. $\Delta^{14}C$ (‰) in wine ethanol (Rheinland-Pfalz, Germany) and in air samples. The results of Vermunt (Austria, May–August 1965–1985), Schauinsland (Germany, July–October 1977–2003), and Jungfraujoch (Switzerland, July–October 1986–2003) have been published by *Levin and Kromer* [2004] and the results of Smilde (The Netherlands, July–October 1975–1994) by *Meijer et al.* [1994]. The Smilde data of the period 1995–2003 (University of Groningen) have not been published before. The Jungfraujoch data of 2004 have been obtained from *Levin et al.* [2008].

2004; *Levin et al.*, 2008; *Meijer et al.*, 1994] and our $\Delta^{14}C$ values of wine ethanol samples from the Rheinland-Pfalz region in Germany. The decreasing trend in our wine results shows good agreement with the atmospheric $^{14}CO_2$ measurements and confirms the conclusion of other wine ethanol studies [*Burchuladze et al.*, 1989; *Martin et al.*, 1995] that wine ethanol is a good indicator of the atmospheric $\Delta^{14}C$ content at a specific measurement site.

[19] As explained before we assume that the measured lower $\Delta^{14}C$ values in the Rheinland-Pfalz region, Smilde and Schauinsland compared to the background sites Vermunt and Jungfraujoch (free troposphere) are entirely due to the dilution of atmospheric $^{14}CO_2$ by regional CO_2-ff emissions. This difference in $\Delta^{14}C$ of a measurement site with the background, which is clearly visible in Figure 2, is our signal, leading to the regional CO_2-ff excess at a measurement site according to equation (4). The difference in $\Delta^{14}C$ between the Rheinland-Pfalz and the background sites has increased since 1965 and is on average −10‰ since 1985. *Levin et al.* [2003] observed a deficit of 10–30‰ in air samples from the city of Heidelberg during summer periods compared to Jungfraujoch. Heidelberg is relatively close to the investigated Rheinland-Pfalz wines areas (distance <100 km). The observed lower $\Delta^{14}C$ values (higher regional CO_2-ff excess) at Heidelberg compared to the Rheinland-Pfalz wine area are expected due to differences in the sampling location (city of Heidelberg versus rural wine area: differences in local CO_2-ff emission rates) and in the daily sampling period (sampling at night in Heidelberg and by day in wine area: differences in atmospheric mixing rates).

[20] Wines that originate from vineyards in the vicinity of nuclear power plants cannot be used for our purpose. We can conclude this from the regional CO_2 excess values we calculated for a part of our investigated wines from the Côtes-du-Rhône region in France. The values are very negative (a CO_2-ff deficit): −1.61 ppm (1993), −38.31 ppm (2001) and −3.96 ppm (2004). We assume that this is due to ^{14}C emissions by nuclear power plants in the vicinity of the investigated wine sites (we do not know the location of the wine sites exactly, but estimate that the distance to nuclear power plants Cruas or Tricastin has been <20 km). The 2001-value is extreme corresponding with a measured $\Delta^{14}C$ value of 195‰, while the $\Delta^{14}C$ value of Jungfraujoch (bg) in 2001 was 83‰. *Martin et al.* [1995] also observed such large $\Delta^{14}C$ values in wine ethanol of the same region. *Levin et al.* [2003] showed an approach to correct for this anomaly in Heidelberg. We could not adopt this approach for our investigated wine regions near nuclear power plants, in France (Côtes-du-Rhône) and Spain (Rioja; Santa Maria de Garona), because we do not have ^{14}C emission and dispersion data in time from the nuclear power plants in these regions. In our research we have investigated for every wine site, whether it was located >50 km from an active nuclear power plant in Europe. We have chosen this distance because we wanted to be sure that our measurement results would not be biased, while we did not know the exact locations of the wine sites and also did not know the exact impact area of a nuclear power plant. The chosen distance might therefore be too large [*Roussel-Debet et al.*, 2006].

2.5. Regional Atmospheric CO_2-ff Excess Values Derived From Wine Measurements

[21] The regional CO_2-ff excess values calculated from our wine measurements give insight in both spatial and annual variations of different sites in Europe within the period July–October. In Figures 3a and 3b the regional CO_2-ff excess (in ppm) derived from the wine ethanol samples of 2003 and 2004 are shown in maps of Europe. The measurement uncertainty in the numbers is about 1 ppm. Different parts of Germany and also the Northern

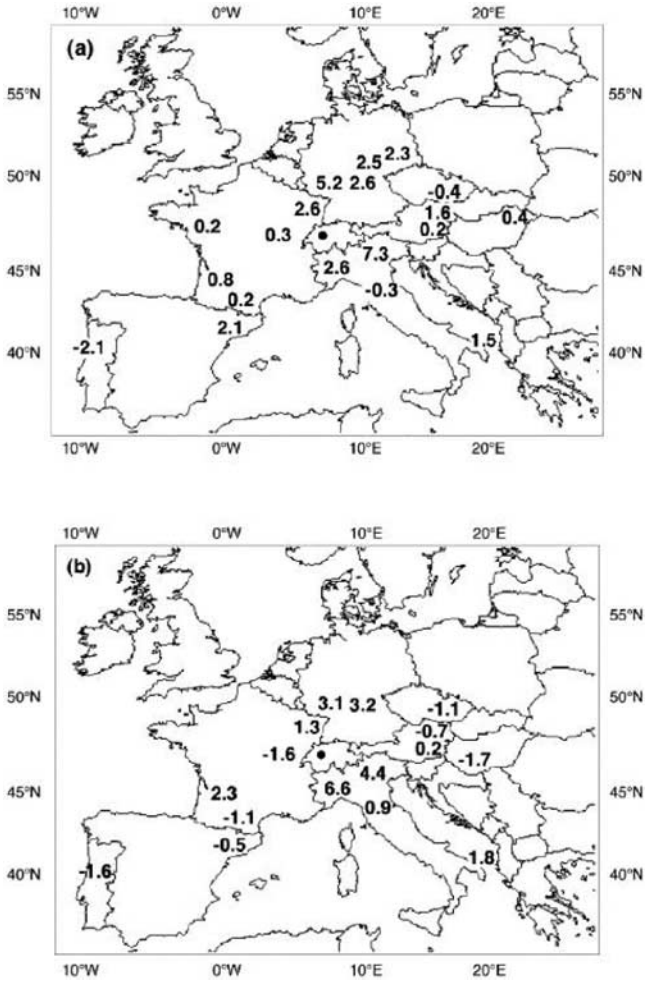

Figure 3. Regional CO_2-ff excess (in ppm) in (a) 2003 and (b) 2004 derived from ^{14}C measurements wine ethanol, relative to the Swiss High Alpine station Jungfraujoch (black dot). The measurement uncertainty in the calculated value is typically 1 ppm.

part of Italy are characterized by a combination of a high-density population, large mobility and intensive industrialization. On the basis of the regional CO_2-ff excess values for both 2003 and 2004 we can distinguish these regions with relatively large values from other regions where the regional CO_2-ff excess values are not significantly different from zero. The differences in regional CO_2-ff excess between regions indeed show a strong relation with the intensity of CO_2-ff emissions in the (vicinity of) specific wine regions. *Hsueh et al.* [2007], who investigated the spatial pattern of ^{14}C in corn leaves in North America during the summer of 2004, also observed this relation. On the basis of our results we can distinguish wine areas in the vicinity of airports and cities (like Barcelona, Lecce and Bordeaux) from more remote regions.

[22] The calculated regional CO_2-ff excess in a specific region varies between successive years. This interannual variation is even better visible in Figure 4, in which the regional CO_2-ff excess for different years is shown for a selection of investigated wine regions. This variation can be due to several factors, like (1) variations in atmospheric mixing and transport at the measurement site and/or the background site, (2) variation in regional CO_2-ff emissions, (3) interannual shifts in the CO_2-sampling period of grapes, (4) the measurement of different wine locations within the same wine region (different local CO_2-ff emissions) and (5) interannual differences in $\Delta^{14}C$ due to other anomalies than regional CO_2-ff emissions at the measurement site and/or the background site that have not been taken into account in the calculation of the regional CO_2-ff excess (as discussed in section 2.3). An example of the latter are probably the negative regional CO_2-ff excess values ($\Delta^{14}C_{wine\ site} > \Delta^{14}C_{bg}$; see equation (4)) we derived from Portuguese wines, which indicate that the tropospheric oceanic atmosphere influencing these measurement sites, has higher $\Delta^{14}C$ values then the free but more continental troposphere at Jungfraujoch and should have been taken into account in the calculation of the regional CO_2-ff excess. This oceanic atmosphere influence is confirmed by measurements at the (elevated) marine site Izaña, Canary Islands [*Levin and Hesshaimer*, 2000]. The negative regional CO_2-ff excess values we derived for several continental European sites in 2004 might also have been due to influences of the oceanic atmosphere or other regional $\Delta^{14}C$ anomalies, introducing a difference between a wine site and the background site (for instance: mountain venting at Jungfraujoch, as mentioned in section 2.3 [*Henne et al.*, 2005]). Correction for these anomalies or using a more representative background site in order to investigate long-term trends in the regional CO_2-ff excess will be subject for further research.

[23] The difference in regional CO_2-ff excess in a specific region over a number of years can be due to a trend in regional CO_2-ff emissions. The Verona wines suggest that this is the case in that region (the 2003 and 2004 results are significantly higher than the 1991 and 1993 ones), but a longer time series is necessary to confirm this. The current investigated time series are for most wine regions too short to observe those long-term trends. The only long-term time series we have at the moment are the wines from the German Rheinland-Pfalz region. Figure 5 shows the regional CO_2-ff excess we derived from wines of 1970–2004, which originated all from the same small area of vineyards (a few hectares) nearby the village Birkweiler (8°07′E, 49°12′W, 230 m asl). Relatively large differences between successive years, up to 5 ppm, can be observed, that complicate the identification of long-term regional CO_2-ff emission trends. *Levin and Rödenbeck* [2007] also observed relatively large interannual variations in the derived regional CO_2-ff excess values from atmospheric $^{14}CO_2$ measurements at Heidelberg and Schauinsland and concluded, based on model simulations, that at least half of this variation can be related to the variation in atmospheric mixing processes. Nevertheless, in spite of the interannual scatter, a clear increasing trend is visible in Figure 5: the average annual regional CO_2-ff excess (with standard error) is 1.38 ± 0.75 (n = 7), 2.45 ± 0.36 (n = 8) and 3.14 ± 0.69 (n = 9) for the periods 1973–1985, 1985–1995 and 1995–2004 respectively. Still, the increase in the regional CO_2-ff excess in the Rheinland-Pfalz area over the decades is no proof that the CO_2-ff emissions in the specific region (or neighboring regions) have increased, at least not at the same rate. Long-term changes in atmospheric mixing and transport processes or in the different regional $\Delta^{14}C$ components, in the specific

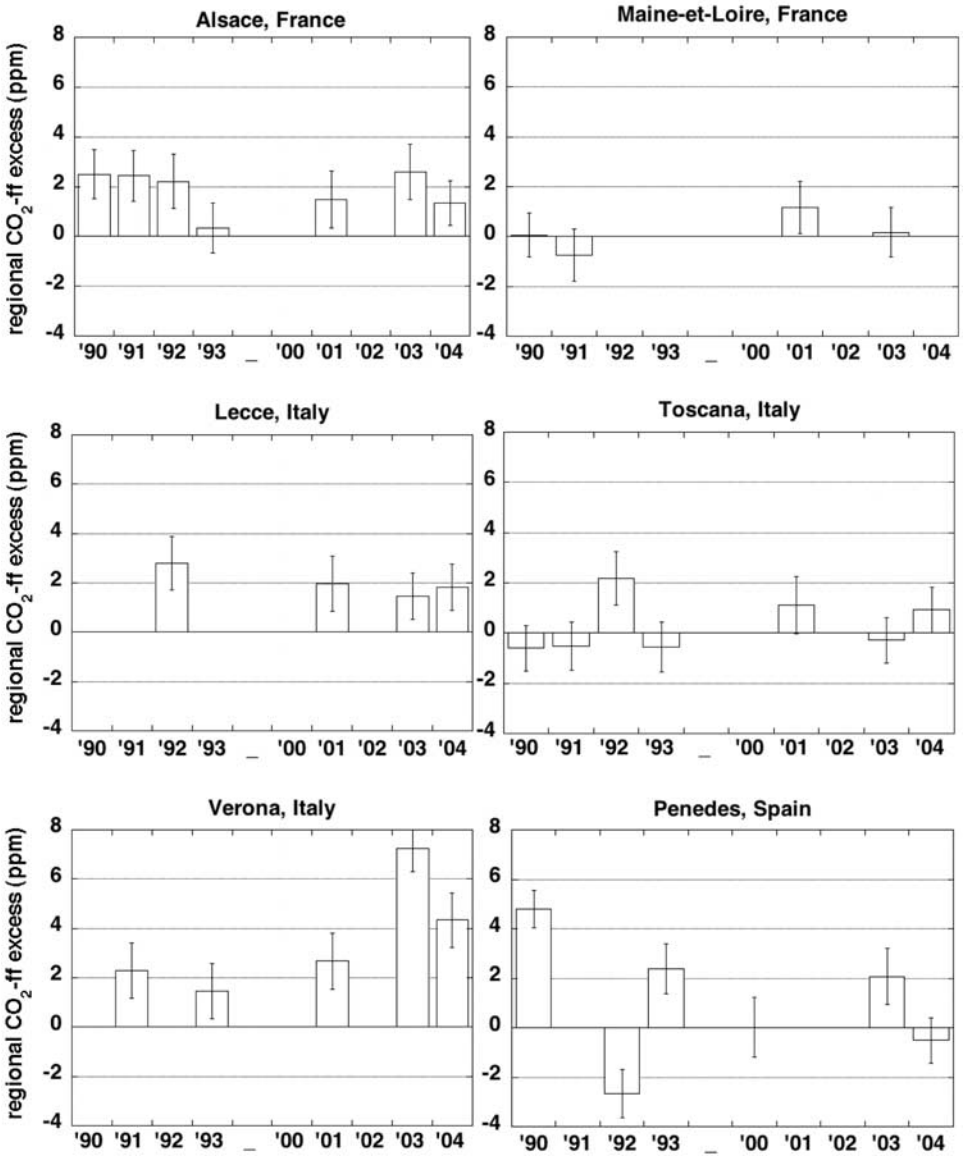

Figure 4. Regional CO_2-ff excess (in ppm) derived from wine ethanol samples, relative to the Swiss High Alpine station Jungfraujoch. The investigated wines of a specific region originate all within a 50 km distance. The measurement uncertainty in the calculated value is typically 1 ppm.

region or at the background site may also contribute to such a trend. Levin and Rödenbeck observed in both observations and modeled simulations of the regional CO_2-ff excess in the period 1998–2006, an increase of almost 1 ppm at Schauinsland (Germany) related to changes in atmospheric mixing. In determining a long-term trend in the regional CO_2-ff excess based on ^{14}C measurements of plant material (like wine ethanol in our case), we should also be aware of the relatively large absolute uncertainties in the calculated regional CO_2-ff excess (up to 1–2 ppm), especially in the period 1965–1990, due to uncertainty in the used average $\Delta^{14}C$ background values, because the period in which the plants have sampled CO_2 is not exactly known (as discussed and estimated in section 2.3). The measurement of plant material from the period 1965–1990 might therefore be less suitable to determine long-term trends.

[24] In spite of the above, the trend in the decadal averages of the German Birkweiler wine makes an increase in fossil fuel consumption in the region likely. The increasing trend, however, does not correspond to the trend in estimated CO_2-ff emissions in the Rheinland-Pfalz area 1990–2004, which shows an increase of CO_2-ff emissions in the period 1990–1995 and then a decrease in the period 1995–2004 [*Statistisches Landesambt Rheinland-Pfalz*, 2008]. For the time periods 1985–1995 and 1995–2004, this would imply that there should not be a large difference (<5%) in the average estimated CO_2-ff emissions between these periods, while our wine measurements show an average increase of 30% (0.7 ppm). Possible explanations for this difference include the influence from neighboring regions (France, other German regions), which have not been taken into account in the particular emission estimates, and the difference in compared time period (average esti-

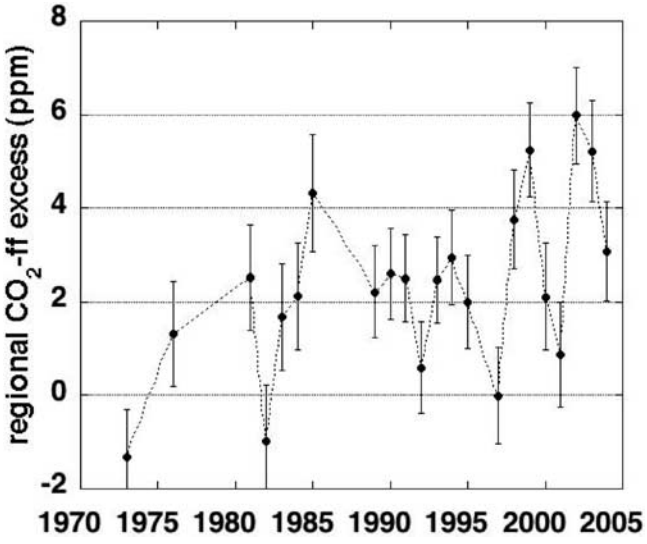

Figure 5. Regional CO_2-ff excess (in ppm) derived from wines from the village of Birkweiler, Germany.

mated emissions of a whole year vs. measured concentrations in summer/autumn period).

[25] The above shows that, in order to determine the long-term trend in CO_2-ff emission fluxes at a specific measurement site to verify the effects of reduction efforts (Kyoto protocol) and to verify emissions inventories, it is essential to (1) perform long-term annual ^{14}C measurements at more European sites, (2) know and quantify all the different factors of the used method that might have influence on this trend, (3) know the area for which a measurement site represents the measured regional CO_2-ff excess and (4) know and quantify all the different factors that influence the $\Delta^{14}C$ value at a measurement site or the background site, like atmospheric mixing and transport processes. A method should be developed to correct the regional CO_2-ff excess for annual and long-term changes in the atmospheric mixing and transport processes. Methods to correct for these kinds of processes include the use of the atmospheric transport tracer ^{222}Rn [*Schmidt et al.*, 2003; *Levin et al.*, 2003]. Unlike wines, there is no way of performing ^{222}Rn measurements back in time, so in our case the use of atmospheric radon measurements is not possible. Another way of correcting is the use of regional (high resolution) atmospheric transport models that simulate the atmospheric mixing and transport of tracers like CO_2 in Europe. These model simulations can be performed, at least in principal, for a long period (1970-current). We have chosen to use the REMO model [*Chevillard et al.*, 2002a, 2002b], and show the comparison between the simulations and our measurements, for the years 2003 and 2004, below.

3. Model—Observation Comparison

3.1. Model Description and Data Selection

[26] The regional atmospheric transport model REMO is based on the regional weather forecast model "Europamodell" of the German Weather Service [*Majewski*, 1991] and additionally includes the physical parameterizations of the global circulation model ECHAM-4 [*Roeckner et al.*, 1996], which are used for this study. REMO (version 5.0) has been extended to an on-line atmospheric chemistry model by implementing modules for the transport of tracers and tropospheric chemical processes [*Langmann*, 2000]. The tracer transport is represented by horizontal and vertical advection, vertical diffusion and convective transport. REMO divides the atmosphere into 20 layers in a hybrid-coordinated system with six layers below 1500 m. The horizontal resolution is 0.5° in a rotated spherical coordinate system, with grid cells of approximately 55×55 km^2. The domain of REMO covers the area north of 30°N. In this study we focused mainly on model results for Western Europe and on the lowest atmospheric layer above ground level (0–60 m). The used boundary conditions for the three years have been derived from the global coarse-grid TM3-model [*Heimann and Körner*, 2003]. REMO simulates its own meteorology inside the domain, but in order to stay close to "reality" it is restarted from ECMWF analyses (European Centre for Medium-Range Weather Forecasts) every day ("forecast mode"), whereas tracer transport is computed continuously [*Chevillard et al.*, 2002b]. The ECMWF analyses contain many surface, upper air and satellite observations and give a representative description of the atmospheric state. For the sake of completeness, we mention that the terrestrial biosphere inside REMO is described using fluxes provided by the Biome-BGC terrestrial ecosystem model [*Churkina et al.*, 2003], and oceanic fluxes are prescribed according to *Takahashi et al.* [1999]. Other studies in which REMO model simulations of atmospheric tracers have been compared with atmospheric observations at different European sites are described by *Chevillard et al.* [2002a] who evaluated the performance of the tracer transport parameterization using ^{222}Rn as a tracer and by *Chevillard et al.* [2002b] who investigated the spatial distribution and temporal variability of atmospheric CO_2 over Europe and western Siberia.

[27] We have used the hourly-simulated CO_2-ff concentrations (this is the total CO_2-ff concentration, not the regional excess) of 2002, 2003 and 2004 from data sets generated by REMO, based on four different emission

Table 1. CO_2-ff Emission Inventories Used to Simulate Atmospheric CO_2-ff Concentrations

Emission Inventory (yr)	Used Abbreviation	Region	Temporal Resolution	Horizontal Resolution	Reference
EDGAR 32FT2000 (2000)	Edg-yr	Global	Yearly	1° × 1°	*Olivier et al.* [2005]
EDGAR 32FT2000 (2000)	Edg-hr	Europe	Hourly	1° × 1°	*Olivier et al.* [2005], *M. Krol* (personal communication, 2007)
IER2000 (2000)	Ier-hr	Europe	Hourly	10 × 10 km	*Pregger et al.* [2007]
Transcom (1998)	Tcc-yr	Global	Yearly	1° × 1°	On the basis of CDIAC NDP-058A, gridded data were obtained for the Transcom Continuous Experiment [*Law et al.*, 2008]

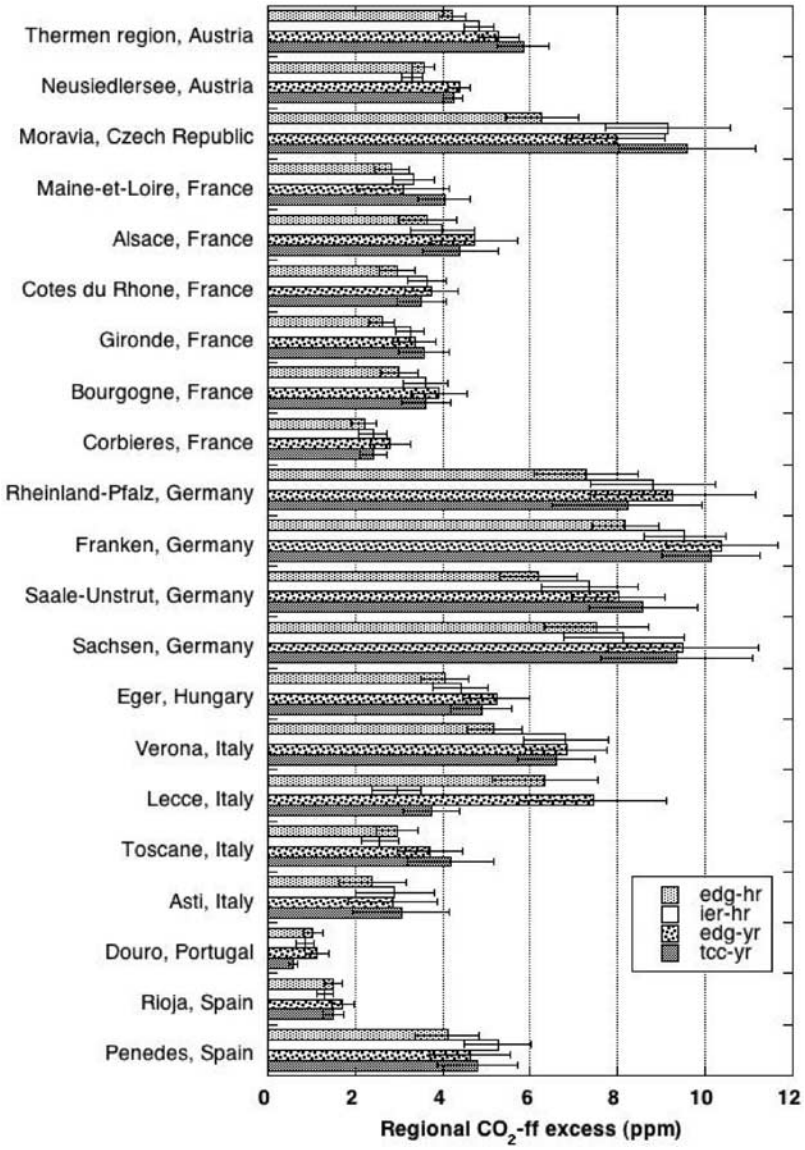

Figure 6. Average regional CO_2-ff excess (ppm) in different European regions (one grid cell per region; day and month averages as explained in the text; error bars show the standard error from these averages) modeled by REMO for 2003 based on four different emission inventories. The regional CO_2-ff excess values simulated for 2002 and 2004 are not shown. These values differ in average −11% and −23% with 2003 but give the same relative differences between the emission inventories.

inventories (Table 1) and the meteorological conditions of 2002, 2003 and 2004. Only the results of 2003 and 2004 have been used for the comparison with the regional CO_2-ff excess values derived from our wine measurements.

[28] In analogy to the observational approach, we have calculated the regional CO_2-ff excess compared to background site Jungfraujoch. The simulated regional CO_2-ff excess is obtained by subtracting the model simulated CO_2-ff concentration at the grid cell corresponding to Jungfraujoch, from the model simulated CO_2-ff concentration of the grid cell corresponding to a specific measurement site. Since the model topography of Jungfraujoch is lower than the site altitude, simulation results from the sixth level above ground level are extracted. The center of the air layer (3182 m asl) is approximately 250 meters below the altitude of the measurement station. This air layer is considered to represent the same air as sampled at atmospheric monitoring station Jungfraujoch.

[29] In order to compare the simulated regional CO_2-ff excess by REMO with those calculated from wine samples, we have made some assumptions about the average sampling period of the grape vines (partly) based on research about the uptake and transport of atmospheric CO_2 and of sugars by grape vines [*Hale and Weaver*, 1962; *Koblet*, 1975; *Alleweldt et al.*, 1975; *Alleweldt*, 1977; *Coombe*, 1992; *van Leeuwen et al.*, 2004]. In analogy to the used measured background values (section 2.3), we have calculated the average simulated regional CO_2-ff excess for the period July–October, with three-fold weight for August and September. The diurnal time periods and moments of CO_2 assimilation by the grapes of our investigated wines are influenced by several variable (climate) factors like light-

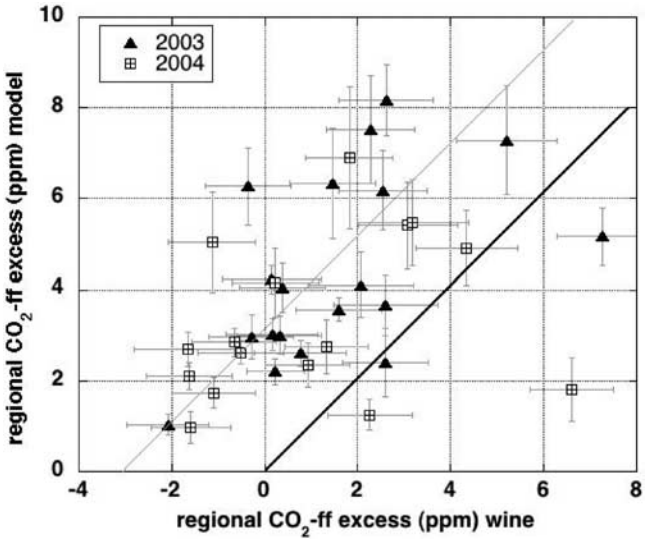

Figure 7. Average regional CO_2-ff excess simulated by REMO, Edg-hr versus the regional CO_2-ff excess derived from wine ethanol of 2003 and 2004, with error bars. The gray line gives an indication of the average deviation from the ideal 1:1 relation (black line).

intensity, temperature and humidity and are not know. Therefore we have used the following approach to obtain simulated average regional CO_2-ff excess values, which can be compared with the measurement results. We have calculated for every month (July–October) the average simulated regional CO_2-ff excess of the diurnal time periods 06:00–20:00 h and 12:00–14:00 h. We have assumed that these periods represent the maximum and minimum diurnal regional CO_2 excess values sampled by the grapes. Also, we assume that the true sampled amounts, which we do not know, will be in between these values. The period 06:00–20:00 h has been based on the period in which the (sun)light intensity (a main factor in the photosynthesis process) might have been high enough for the grapevines to assimilate CO_2 in the respective growing period. The period 12:00–14:00 h has been based on the diurnal period when, because of atmospheric mixing, the atmospheric CO_2 concentration is in general the lowest [*Chevillard et al.*, 2002b]. The differences between the monthly average regional CO_2-ff excess values of the two diurnal periods give an indication of how critical the precise choice of the time period is for the model results. Typically, the average simulated regional CO_2-ff excess for the period 06:00 h–20:00 h is 25% higher than for the period 12:00 h–14:00 h.

[30] We have calculated the average simulated regional CO_2-ff excess for all the grid cells in which the investigated wine areas of 2003 and 2004 are located. The uncertainty in the values has been based on the uncertainty (standard error) in the average diurnal and annual sampling period (obtained as described above). In the simulations the fossil-fuel emissions have been chosen identical for all years. Any interannual variability is therefore caused solely by variability in atmospheric mixing and transport.

3.2. Simulated Regional CO_2-ff Excess by REMO

[31] Figure 6 shows the average regional CO_2-ff excess in 2003 simulated by REMO using the four different emission inventories (see Table 1) for the different investigated European wine regions. In comparison with the average results of REMO using emission inventory "edg-hr" for the different measurement sites, the results obtained with "ier-hr" are in average 11% higher, "tcc-yr" +19% and "edg-yr" +25%. The simulated CO_2-ff concentrations for emission inventories "edg-hr" and "ier-hr" are in general the lowest, because in these emission inventories the seasonal (summer/winter) and diurnal variations in CO_2-ff emissions have been taken into account, while the CO_2-ff emissions in "tcc-yr" and "edg-yr" are constant in time. Since we measure in the summer period when the regional CO_2-ff emissions are usually relatively low, "tcc-yr" and "edg-yr" yield too high regional CO_2-ff excess values. The differences between the emission inventories can also be due to several other factors, like differences in the estimated emissions of a country or differences in the spatial patterns of the emission inventories. In the latter case, the results of different emission inventories, are based on (slightly) different areas with more or less CO_2-ff emission sources (like a city, or the sea). In the regions Moravia (Czech Republic) and Lecce (Italy) the relatively large differences between the results of "edg-hr" and "ier-hr" (+43% and −54% for "ier-hr" respectively), might be an indication for one of the just mentioned factors.

3.3. Results and Discussion of Model—Observation Comparison

[32] In Figure 7 we have plotted the regional CO_2-ff excess simulated by REMO (Edg-hr) against the regional CO_2-ff excess derived from our wine-measurements. The black line shows the ideal 1:1 relation. Even though there is considerable scatter, there is a clear systematic difference between model and observations. The REMO simulations show an average bias of almost +3 ppm.

[33] The observed differences between the model and observations can be due to many different factors in both the method to derive the regional CO_2-ff excess from ^{14}C wine ethanol measurements as in the model simulation. Although we used emission inventories of 1998 and 2000, which might not have been representative for 2003 and 2004, it cannot explain the difference of +3 ppm we observed. It would imply a decrease of a few 100% in the CO_2-ff emissions within a few years in some regions. On the basis of the statistics of the German Rheinland-Pfalz region (mentioned in section 2.5 [*Statistisches Landesambt Rheinland-Pfalz*, 2008]), we think that is not realistic. A few probable factors that can cause such a systematic deviation between the measurement and model results are related to the chosen background site Jungfraujoch. Firstly, (part of) the systematic deviation might be due to the use of too low simulated CO_2-ff concentrations of Jungfraujoch, caused by difficulties in the REMO model to simulate the atmosphere processes at elevated mountain sites, like mountain venting [*Henne et al.*, 2005]. *Chevillard et al.* [2002a] observed in the comparison of measured and REMO-simulated ^{222}Rn concentrations that the atmospheric ^{222}Rn concentrations at elevated (mountain) sites were difficult to simulate. Secondly, the background $\Delta^{14}C$ values of Jungfraujoch we have used for 2003 and 2004, might have been too low because of regional $^{14}CO_2$ influences at the background site. In that case, Jungfraujoch has not been representative for the free

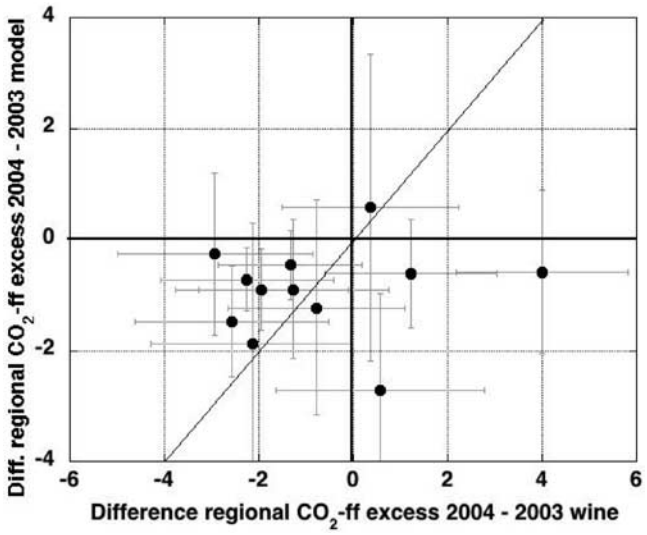

Figure 8. Difference in regional CO_2-ff excess (in ppm) between 2004 and 2003 for the wine results and the REMO results (Edg-hr).

(continental) troposphere. These are clearly disadvantages of using the Jungfraujoch site as background site for the determination of the regional CO_2-ff excess. The ideal background site would therefore be a lowland site with no local and regional CO_2-ff emissions. The use of other background sites in Europe is an important topic for further research in order to identify trends in regional CO_2-ff excess values.

[34] Since the regional CO_2-ff excess at a wine measurement site is not necessarily representative for the average regional CO_2-ff excess of a region of 55 $\times$ 55 km^2 as is simulated by REMO, this might also have contributed to the observed deviation between the measurement and model results. The, usual rural, wine sites might well be systematically "cleaner" than the average of the region. *Chevillard et al.* [2002a] observed that site-specific effects, such as local emission sources and local topography, biased simulated regional CO_2-ff excess values because these factors were difficult to capture in the used resolution of models (same resolution as we used: 55 $\times$ 55 km^2). Atmospheric transport models and emission inventories with a higher resolution are therefore needed.

[35] Other factors that might have contributed to the observed systematic deviation between the modeled and observed results of a measurement site are (1) wrong estimations of the emissions for a certain grid cell which influence the simulated regional CO_2-ff excess, (2) assumptions we have made in the calculation of the regional CO_2-ff excess about the used background CO_2 concentration and other regional $^{14}CO_2$ sources (as described in section 2.3 and also mentioned in section 2.5) and (3) the estimated average time period (monthly and diurnal) in which grapes have assimilated ("sampled") CO_2.

[36] We have compared the differences in regional CO_2-ff excess between 2003 and 2004 for the observations and the model for different regions, to investigate the simulation of interannual variations by REMO. This is shown in Figure 8. The difference between the model results of 2003 and 2004 (calculated as "2004" – "2003") is (in our case) only due to differences in the atmospheric mixing between both years. The simulated regional CO_2-ff excess values of 2004 are in most regions approximately 1 ppm lower compared with 2003, while the differences between 2003 and 2004 in the observations in these same regions are approximately 2 ppm lower compared to 2003. When we consider that the differences between 2003 and 2004 in the observations are not only due to changes in atmospheric mixing alone, but also to other factors (see section 2.5: interannual variation in CO_2-ff emissions, the sampling period of the grapes, the regional sampling location and differences in $\Delta^{14}C$ due to other anomalies than regional CO_2-ff emissions at the measurement site and/or the background site) and we assume that the REMO simulations of atmospheric mixing are correct, then we may conclude that a considerable part (in this case approximately 50%) of the total interannual variation in the regional CO_2-ff excess can be corrected for using REMO simulations. This is a fortunate fact, since it enables us to use REMO to interpret our observations through the years (Figure 5) in view of the effects of atmospheric transport and mixing and eventually correct for this. After this kind of correction, our observations are a more direct measure for the regional fossil fuel emissions and its trends within Europe. Recently, *Levin and Rödenbeck* [2007] demonstrated the use of model-simulated data in this fashion, using TM3 as atmospheric transport model. This model, however, has a much lower resolution than REMO. Since REMO simulations are at the moment only available for a few years, we cannot yet compare a long-term trend.

4. Discussion: ^{14}C in Wine Ethanol and Other Plant Materials as Proxy for Atmospheric $^{14}CO_2$

[37] As we described in the introduction, several studies already showed the use of ^{14}C measurements in annual plant material as a proxy for atmospheric $^{14}CO_2$. In this paper we also show the good comparison of the $\Delta^{14}C$ values of our wine ethanol samples of German wines from the Rheinland-Pfalz region with air measurements from different other regions in Europe in the period 1965–2004 (Figure 2). Beside the main advantage of (annual) plant material that it is widely available and can be obtained from many different areas, several differences with atmospheric measurements appear, which can be considered as disadvantages and need to be taken into account when using the ^{14}C as a proxy for atmospheric $^{14}CO_2$. *Hsueh et al.* [2007] discuss this as well in their study about ^{14}C measurements in corn leaves. An important difference with atmospheric sampling is that the period in which $^{14}CO_2$ has to be sampled (assimilated) by the plants is not adjustable. The sampling period is therefore not known and it is also limited to only a part of a day (daylight) and part of the year (mainly spring and summer). Another disadvantage is that other carbon components (than freshly assimilated CO_2), which may contain assimilated atmospheric ^{14}C from earlier sampling periods (previous years), can "pollute" the sample (plant) material. This is only the case when plants (or the investigated parts) also take up carbon via other ways than photosynthesis.

[38] Several advantages and disadvantages can be identified as well in a comparison of different plant materials that can be used as a proxy for atmospheric $^{14}CO_2$. As explained

in the introduction we choose wine ethanol as sample material, partly for practical reasons but also because wine ethanol of previous years can be measured, giving the opportunity to investigate historic trends in the regional CO_2-ff excess (as long as suitable background data is available). The main disadvantage of using wine ethanol we have observed, is the lack of sample information about the content and the origin of the grapes (exact locations) when only the label on the wine bottle is available. This was the case for all our investigated wines, except the German Rheinland-Pfalz wines of the village Birkweiler (Figure 5). These latter wines were directly obtained from the specific wine-farmer and the wine-areas are exactly known. For these wines we also know that they are not from mixed harvest years and no sugar was added in the wine-making process. For all the other wines, we do not know whether the wines were, legally or not, mixed or contained alcohol from other sugar (and atmosphere) sources, what might have biased our calculated regional CO_2-ff values. We have not identified vintage fraud: in which the harvest year mentioned on the bottle of the wine is not the true harvest year. This can be identified based on differences in atmospheric ^{14}C concentrations between different harvest years due to the decreasing atmospheric ^{14}C concentration after the nuclear bomb tests in the 1960s. Because the decrease rate has decreased since the mid-1960s and approaches since the mid-1990s the measurement uncertainty of the ^{14}C measurements, it is not a very suitable tool anymore to identify vintage fraud [*Martin et al.*, 1995]. On the basis of the lack of information about the wine content and origin that we had in our approach, we conclude that it is more fruitful to select a single vineyard locally and obtain information about the wine making process and the location of the vineyard from the specific wine farmer, than to simply purchase wine from a certain region in local shops.

[39] We have measured the ^{14}C content of wine ethanol instead of the wine to assure that we almost only measured carbon from the grape sugars, which we consider as proxy for atmospheric $^{14}CO_2$ of the respective growing period of the grapes (this only holds if no sugar is added in the wine-making process). Since, based on the measured density of our distilled wine ethanol samples, the contribution of other distilled carbon-containing components was not measurable, we think that we have safely assumed that the ^{14}C contribution of these components has also been negligible. In the case of measuring other plant materials it might be more difficult to be assure that no other carbon-sources than recent assimilated atmospheric $^{14}CO_2$ have contributed to the measured ^{14}C content of the sample. This might, for instance, be the case if ^{14}C in tree-rings are used as a proxy for atmospheric $^{14}CO_2$. Tree-rings are, like wine ethanol samples, potentially useful to obtain long-term measurement series of ^{14}C from previous years. A comparison by *Levin and Kromer* [1997] of ^{14}C measurements of tree-rings and air samples at the German site Schauinsland in the period 1974–1986 showed good comparison if the average value of the air samples over the months May–August was taken. However, in comparison with the carbon from wine ethanol, which origins almost completely from wine grapes that assimilated CO_2 during one year (as is very well known from many research studies, among others: *Hale and Weaver* [1962] and *Koblet* [1975]), the carbon content of a one-year tree-ring shows intra-annual variation, which is probable not only related to variation in CO_2 uptake by photosynthesis, but also to for instance the input of starch (form earlier years) [*Rocha et al.*, 2006]. More research is therefore needed to identify the contribution of different carbon-sources to the total ^{14}C-content of tree-rings. Main advantages of using ^{14}C measurements of tree-rings in comparison to wine ethanol samples, are the ability to investigate many more different sites in whole Europe and, in those cases a annual tree-ring consists of seasonal sequences, it might give more information about seasonal differences in the atmospheric $^{14}CO_2$ content (as long as the contribution and seasonal-variation from other carbon sources is also well-known). Since both wine ethanol and tree-rings have their specific disadvantages, it might be interesting to investigate the long-term ^{14}C-content of tree-rings and wine ethanol samples from the same measurement site (a tree near a vineyard) and (if possible) compare these results with atmospheric $^{14}CO_2$ measurements from the same location.

5. Conclusions

[40] The measurement of ^{14}C in wine ethanol of different European regions and different harvest years gives insight into the temporal and spatial distribution of atmospheric $^{14}CO_2$ concentrations in Europe that can be directly related to regional and/or local CO_2-ff emissions. An important advantage of the measurement of wines is that the atmosphere and also its changes can be monitored annually back in time. This can be very helpful in the investigations of long-term trends in regional atmospheric CO_2-ff excess at different sites in Europe. The measurement of ^{14}C in wines of a known location is a relatively easy way to supplement atmospheric measurement sites where CO_2-ff concentrations can be determined. The main disadvantage of using $\Delta^{14}C$ measurements of wine ethanol as a proxy for atmospheric $^{14}CO_2$ is the unknown diurnal and monthly sampling period. This also holds for other annual plant samples. In the calculation of the regional CO_2-ff excess this unknown sampling period introduces an uncertainty in the used average background $\Delta^{14}C$ values, which adds, especially in the period 1965–1990, significantly to the total uncertainty in the calculated regional CO_2 excess value. Our approach might therefore not be very useful for long-term investigations before 1990.

[41] The interannual variation and the long-term trend in the atmospheric regional CO_2-ff excess derived from the ^{14}C measurement in wine ethanol at a particular site or area are mainly dependent on the interannual variation and trends in the following factors: (1) the meteorology: atmospheric mixing and transport processes, (2) the $\Delta^{14}C$ value of the background location, (3) the relative regional contribution of the ocean and biosphere CO_2 sources to the ^{14}C of a site and finally (4) local/regional CO_2-ff emissions.

[42] Obviously, (4) is the signal we are looking for and we have to design a proper procedure to address the other points. As a first attempt toward such a procedure, we compared our CO_2-ff observations to simulations by the regional atmospheric transport model REMO to address point (1). Although the model results show an average bias of almost +3 ppm compared to the observations, both model

and observation results show a decrease in CO_2-ff concentration between 2003 and 2004. On the basis of our first results we can conclude that by using REMO at least part of the interannual variation in the observed regional CO_2-ff excess values can be corrected for a non-CO_2-ff emission related factor: atmospheric mixing and transport. The net result from this exercise then gives a CO_2-ff signal that is potentially useful for the verification of trends in regional fossil fuel emissions. Further research to address points (1), (2) and (3) for a long-term period is, however, necessary. For REMO, too few years of output are available at present to completely perform this exercise. Long-term results are available from the world-wide grid model TM3 [*Levin and Rödenbeck*, 2007], but in order to use them for our observations the model output has to be adapted for the average sampling pattern of our wine grapes first (sufficient time and spatial resolution is necessary).

[43] To investigate long-term trends in regional CO_2-ff emissions more long-term annual ^{14}C-measurements should be performed in different regions, in Europe and elsewhere. On the basis of our experiences using wine ethanol, it is more fruitful to select a single vineyard locally and obtain information about the wine content from the specific wine farmer, than to simply purchase wine from a certain region in local shops with no information about the exact content of the wine and origin of the wine grapes. In the first case, information about the wine content and the exact origin of the vineyard locations can be obtained and secondly locations can be selected with care, in order to avoid large local CO_2-ff sources (motorways, factories, conventional power plants) and nuclear power plants in the vicinity. Doing so, one eliminates the uncertainties about the content of the wines (added sugars, mixing of different harvest years) and one avoids scatter in (interannual) data because of different local conditions in the same region. Since wine regions do not cover all European countries, it is recommended to use other plants as atmospheric $^{14}CO_2$ samplers as well (like tree rings as investigated by *Levin and Kromer* [1997] or corn leaves, as investigated by *Hsueh et al.* [2007]). The monitoring back in time, could in the case of annual plants like corn leaves, however, be difficult. To address the atmospheric regional CO_2-ff excess in different periods of the year, and not only in the period of July–October as with wines, it should be investigated which plants might be useful atmospheric samplers for this purpose.

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